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(54) NEGATIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY AND MANUFACTURE THEREOF AND THE LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode material for realizing a lithium secondary battery having a high discharge capacity and a high speed charge and discharge characteristic while restricting the decomposition of the electrolyte solvent and provide a lithium secondary battery using this negative electrode material.

SOLUTION: In this method mixture gas composed of the organic material and the inert gas and including the organic material at 2-50% of mole concentration is used and chemical deposition is performed to the graphite grains in a fluidized bed reaction furnace at 900-1200°C. A negative electrode material for lithium secondary battery formed of the graphite grains and a crystalline carbon layer for coating the whole surface of the graphite grains of which the whole surface is arranged in parallel with a carbon 110 face of the carbon layer is thereby formed.

CLAIMS

[Claim(s)]

[Claim 1] A negative pole material for lithium secondary batteries wherein it consisted of a

graphite-grains child and a crystalline carbon layer which covers all the surfaces of said graphite-grains child and all the surfaces of said graphite-grains child are covered with the 110th page of carbon.

[Claim 2]The negative pole material for lithium secondary batteries according to claim 1 in which a ^7Li -NMR spectrum of a negative pole material which carried out the intercalation of the lithium ion has an absorption spectrum in 40-50 ppm of a lithium-chloride standard chemical shift and 10-20 ppm.

[Claim 3]The negative pole material for lithium secondary batteries according to claim 1 whose average spacing d_{002} of a carbon layer is less than 0.337 nm.

[Claim 4]The negative pole material for lithium secondary batteries according to claim 1 which a carbon layer shows optical anisotropy under a polarization microscope.

[Claim 5]The negative pole material for lithium secondary batteries according to claim 1 using natural graphite as a graphite-grains child.

[Claim 6]A lithium secondary battery formed using the negative pole material according to any one of claims 1 to 5.

[Claim 7]By carrying out chemical vapor deposition treatment of the graphite-grains child using mixed gas of organic matter gas or an organic matter and inactive gas in a fluidized bed reactorA manufacturing method of a negative pole material for lithium secondary batteries which consists of a crystalline carbon layer which covers the surface of a graphite-grains child forming a carbon layer in a graphite-grains child's surface and said graphite-grains child and in which said graphite-grains child has the 110th page of parallel carbon of the surface and said carbon layer.

[Claim 8]A manufacturing method of the negative pole material for lithium secondary batteries according to claim 7 whose chemical-vapor-deposition-treatment temperature molar concentration of an organic matter in mixed gas is 900-1200 °C at 2 to 50%.

[Claim 9]A manufacturing method of the negative pole material for lithium secondary batteries according to claim 7 using natural graphite as a graphite-grains child.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is large scale is high potential and relates to the negative pole material which can manufacture the lithium secondary battery which was excellent in the charge-discharge cycle characteristic and prevented disassembly of the electrolysis solution its manufacturing method and the lithium secondary battery provided with the negative pole material.

[0002]

[Description of the Prior Art]High-energy-density-ization of the cell is demanded in connection with the small weight saving of an electronic device. Also from the field of saving resources development of the highly efficient rechargeable battery in which repetition charge and discharge are possible is demanded. The lithium secondary battery excellent in high energy density a light weight small size and a charge-discharge cycle characteristic is conventionally proposed for the purpose of meeting such a demand.

[0003]A lithium secondary battery is classified into a rechargeable lithium-ion battery a

lithium polymer secondary battery a totally-solid lithium secondary battery etc. according to an electrolytic kind. Among these rechargeable batteries a rechargeable lithium-ion battery is a rechargeable battery with which development is continued in order to solve the problem inferior to boost charge nature and the problem that a cycle life is short which a lithium metal secondary battery has the problem inferior to safety etc.

[0004] As for the lithium metal secondary battery the lithium metal is used for the anode. On the other hand the rechargeable lithium-ion battery is having the carbon material used for an anode. By using a carbon material for an anode it is going to solve the above-mentioned demand. That is if the rechargeable lithium-ion battery which constituted the cathode from a lithium compound and constituted the anode from a carbon material charges this in an anode a lithium ion will be doped by the carbon material and the compound between what is called carbon-lithium layers will be formed. On the other hand at the time of discharge a lithium ion [DOPINKU / between / the layers of a carbon material / de] a lithium ion and the lithium ion [DOPINKU / lithium ion / de] moves to a cathode again and returns to a lithium compound. By such a mechanism the rechargeable lithium-ion battery can carry out repetition charge and discharge.

[0005] As an anode used for a rechargeable lithium-ion battery there are a black lead system anode and a carbon system anode. In the cell constituted using these anodes when practicality is disregarded and it performs prolonged discharge the service capacity of a carbon system anode is 600 or more mAh/g. This service capacity is large as compared with 350 - 370 mAh/g of the service capacity on the practical service condition of a black lead system anode. However in a practical service condition the service capacity of a carbon system anode is 250 - 300 mAh/g and is a value lower than 350 - 370 mAh/g of the service capacity on the practical service condition of a black lead system anode. A carbon system anode has the low density of a carbon material and its discharge pressure is also low. For this reason compared with the cell which used the black lead system anode spark discharge energy is also inferior in the cell using a carbon system anode.

[0006] From the above Reason the black lead system anode is used in many rechargeable lithium-ion batteries.

[0007] In order to perform charge and discharge efficiently for a short time in the case of the rechargeable lithium-ion battery using a black lead system anode it is desirable for black lead which is a constituent particle of a black lead system anode to be particles. By atomizing black lead the surface area in which contact with black lead and an electrolysis solution is possible within a cell increases and it is thought that transfer of the lithium ion between an electrolysis solution and black lead becomes easy as a result.

[0008] This invention persons inquired about atomizing the black lead used for the anode of a rechargeable lithium-ion battery. As a result the increase in the service capacity of a cell was accepted with atomization of black lead. However the charge required for a cell also increased with atomization of black lead and it found out that coulomb efficiency fell as a result. It found out the reactivity of black lead and the solvent which constitutes the electrolysis solution of a cell becoming high with atomization of black lead and a solvent decomposing as a result and raising generating of gas remarkably. If gas is emitted in the sealed cell the danger that the internal pressure of a cell will go up and a cell will explode will increase. Therefore it is very important to control generating of gas in the inside of a cell.

[0009] Generally the main solvent of the electrolysis solution used for a rechargeable

lithium-ion battery has much carbonic esters such as ethylene carbonate (it abbreviates to EC below) and propylene carbonate (it abbreviates to PC below). To these main solvents addition mixing of the electrolytes such as LiPF_6 or LiBF_4 was carried out and the electrolysis solution has been obtained. The Reason many solvents such as PC and EC are used as a main solvent of an electrolysis solution is that these solvents have high specific inductive capacity and the desirable solvent characteristics such as a wide operating temperature range. PC is a solvent which can be used at low temperature especially. However if the electrolysis solution and black lead system anode which contain PC as mentioned above are made to live together in a cell PC will decompose and gas will be generated. Disassembly of PC is a phenomenon seen only when using black lead for the anode of a cell. It is a phenomenon which is not seen when using a carbon system anode. [0010] Thus in a cell if the electrolysis solution and black lead system anode containing PC are made to live together PC will decompose. As a result the danger that not only the coulomb efficiency of a cell falls but the internal pressure of a cell will go up and a cell will explode increases. For this reason it is anxious for development of the black lead system anode which does not produce decline in coulomb efficiency i.e. the high black lead system anode of PC-proof nature without PC decomposing even if it uses for the electrolysis solution containing PC.

[0011] The method of controlling disassembly of PC is proposed by covering a graphite-grains child's surface with the low crystal carbon which does not disassemble PC conventionally.

[0012] How (the patent No. 2643035 gazette) to use the composite material which covered black lead with low crystal carbon using chemical vapor deposition as such an example as a negative pole material How (JPH5-121066A) to use the composite material in which average spacing d_{002} covered black lead with carbon of 0.337 nm or more as a negative pole material And the method (JPH5-275076A) of using the composite material which covered black lead with amorphous carbon as a negative pole material is mentioned.

[0013] The anode using the composite material obtained by these methods controls disassembly of PC. However the cell using these composite materials as an anode As compared with the cell using the anode which comprised only a graphite-grains child who has not covered low crystal carbon the problem which originates in low crystal carbon originally [-- that service capacity is low and high-speed charge and discharge cannot be performed --] will be added on a practical service condition.

[0014] In the carbon system anode or black lead system anode used for a rechargeable lithium-ion battery it has the problem to which a carbon system anode originates the problem to which a black lead system anode originates in black lead system material in a carbon system material and these problems conflict mutually. Therefore it is anxious for development of the negative pole material for rechargeable lithium-ion batteries which solves these problems simultaneously and the rechargeable lithium-ion battery using the negative pole material.

[0015]

[Problem to be solved by the invention] This invention persons evaluated the black lead-graphite composite obtained by covering black lead with carbon under various conditions as a negative pole material for rechargeable lithium-ion batteries using chemical vapor deposition. As a result when using the composite material which covered the surface of

black lead with crystalline carbon uniformly and thoroughly as an anode of a rechargeable lithium-ion battery this anode controls disassembly of PC etc. certainly and. The cell obtained has high service capacity high-speed charge is possible and this anode found out having the electrode performance superior to the negative pole material covered with conventional low crystal carbon.

[0016] The above-mentioned negative pole material found out that it could use for all of lithium secondary batteries such as a lithium polymer secondary battery a totally-solid lithium secondary battery and a rechargeable lithium-ion battery.

[0017] The ^7Li -NMR spectrum of the above-mentioned negative pole material which carried out the intercalation of the lithium ion was measured. And as a result of examining this ^7Li -NMR spectrum it found out that this ^7Li -NMR spectrum could be used for evaluation of the crystallinity of the above-mentioned negative pole material. This invention was completed based on these results.

[0018] Therefore an object of this invention is to provide the negative pole material which can realize the lithium secondary battery in which solve many above-mentioned problems and disassembly of an electrolysis solution solvent is controlled and service capacity is high and high-speed charge and discharge are possible its manufacturing method and the lithium secondary battery formed using the negative pole material.

[0019]

[Means for solving problem] To achieve the above objects this invention is a proposing following things thing.

[0020] [1] The negative pole material for lithium secondary batteries which having consisted of a graphite-grains child and a crystalline carbon layer which covers all the surfaces of said graphite-grains child and covering with all the surfaces of said graphite-grains child and the 110th page of carbon of said carbon layer.

[0021] [2] The ^7Li -NMR spectrum of the negative pole material which carried out the intercalation of the lithium ion has an absorption spectrum in 40-50 ppm of a lithium-chloride standard chemical shift and 10-30 ppm. The negative pole material for lithium secondary batteries given in [1].

[0022] [3] Average spacing d_{002} of a carbon layer is less than 0.337 nm. The negative pole material for lithium secondary batteries given in [1].

[0023] [4] A carbon layer shows optical anisotropy under a polarization microscope. The negative pole material for lithium secondary batteries given in [1].

[0024] [5] Natural graphite is used as a graphite-grains child. The negative pole material for lithium secondary batteries given in [1].

[0025] [6] [1] or The lithium secondary battery formed using the negative pole material given in any of [5] they are.

[0026] [7] By carrying out chemical vapor deposition treatment of the graphite-grains child using the mixed gas of organic matter gas or an organic matter and inactive gas in a fluidized bed reactor A manufacturing method of the negative pole material for lithium secondary batteries which consists of a crystalline carbon layer which covers all the surfaces of the graphite-grains child forming a carbon layer in all the surfaces of a graphite-grains child and said graphite-grains child and in which said graphite-grains child has the 110th page of parallel carbon of the surface and said carbon layer.

[0027] [8] At 2 to 50% the molar concentration of the organic matter in mixed gas is [chemical-vapor-deposition-treatment temperature] 900-1200 **. A manufacturing

method of the negative pole material for lithium secondary batteries given in [7].

[0028][9] Natural graphite is used as a graphite-grains child. A manufacturing method of the negative pole material for lithium secondary batteries given in [7].

[0029] Hereafter this invention is explained in detail.

[0030]

[Mode for carrying out the invention] The negative pole material for lithium secondary batteries of this invention is a black lead-graphite composite which consists of a graphite-grains child and a carbon layer which covered the surface. Said carbon layer is crystalline carbon which can be formed by chemical vapor deposition treatment and which has predetermined molecular orientation.

[0031] Although there are also submaterials such as a paste and a conducting material as a "negative pole material" of a lithium secondary battery besides the negative pole material of the carbon system which is a charge of a main material or a black lead system. In this invention in particular in calling it the "negative pole material" of a lithium secondary battery as long as there is no notice the negative pole material of the carbon system which is a charge of a main material or a black lead system shall be pointed out.

[0032] As for average spacing d_{002} although natural graphite or an artificial graphite may be sufficient as the black lead used for a graphite-grains child's raw material it is desirable that it is a thing of 0.336 nm or less of high crystallinity. As for black lead of a raw material it is desirable to have ground in diameter of grain of maximum size of 100 micrometers or less. 5-30 micrometers of mean particle diameter are preferred and it is 10-20 micrometers more preferably.

[0033] As the method of grinding of black lead which methods such as the publicly known impact crushing method and the grinding method may be used. As for the tap density of the graphite-grains child after grinding although restriction in particular does not have it when the ease of handling is taken into consideration it is desirable that it is more than 0.7 g/cm^3 . When the tap density of the graphite-grains child after grinding is less than 0.7 g/cm^3 the handling by carrying out compression processing so that tap density may become about this graphite-grains child by compactor roller mill disc mill or a vibration mill more than 0.7 g/cm^3 easily.

[0034] After mulling a graphite-grains child with a pitch or resin and covering him as a method of covering a graphite-grains child with carbon and forming a carbon layer in a graphite-grains child's outside surface the method of carbonizing this mull coating and the fixed-bed chemical-vapor-deposition-treatment method of the standing type are known.

[0035] A crack and exfoliation occur on the carbide surface by contraction produced when the pitch and resin which were covered carbonize and the method of carbonizing a pitch or resin and black lead after mull covering cannot cover a graphite-grains child with carbon thoroughly.

[0036] The fixed-bed chemical-vapor-deposition-treatment method of a standing type is the method of heating more than the pyrolysis temperature of an organic matter settling a graphite-grains child on the black lead board which it had for example into the quartz tube and supplying the mixed gas which consists of an organic matter used as a carbon source and dilution gas in a quartz tube. In this method a graphite-grains child is covered with carbon only the portion which mixed gas and a graphite-grains child contact. Therefore when processing a graphite-grains child by a fixed-bed chemical-vapor-deposition-treatment method the portion with which many are not covered by the

graphite-grains child surface is left behind. Therefore depending on the fixed-bed chemical-vapor-deposition-treatment method of a standing type a graphite-grains child may be unable to be thoroughly covered with carbon.

[0037] To these coating methods the chemical-vapor-deposition-treatment method of a fluidized bed can cover a graphite-grains child's outside surface with carbon simply and thoroughly and moreover crystalline carbon vapor-deposits it mainly on the graphite-grains child surface (it abbreviates to vacuum evaporated carbon hereafter). Therefore as for chemical vapor deposition treatment it is desirable to carry out using a fluid bed reactor. By performing chemical vapor deposition treatment using a fluid bed reactor chemical vapor deposition treatment can be carried out in large quantities efficiently. A graphite-grains child's surface can be uniformly covered with vacuum evaporated carbon.

[0038] In the chemical vapor deposition treatment of a fluidized bed the graphite-grains child in a fluid bed reactor forms the fluid bed. The bulk density of the fluid bed has desirable $0.1 - 0.5 \text{ g/cm}^3$.

[0039] As for chemical-vapor-deposition-treatment temperature $850-1200^\circ\text{C}$ is preferred a more desirable temperature is $900-1200^\circ\text{C}$ and a more desirable temperature is $950-1150^\circ\text{C}$. When chemical-vapor-deposition-treatment temperature is less than 850°C its deposition rate of pyrolytic carbon is small and although it changes with kinds of organic matter as a carbon source used when processing since chemical vapor deposition treatment takes a long time to chemical-vapor-deposition-treatment temperature it is not preferred [temperature].

[0040] The conversion rate to carbon of an organic matter becomes high as chemical-vapor-deposition-treatment temperature becomes high. However if chemical-vapor-deposition-treatment temperature exceeds 1200°C it will grow up that vacuum evaporated carbon is fibrous or in the shape of [protean] soot and will become difficult to grow up in the shape of a film. For this reason in this invention aiming at formation of the film of the shape of a uniform film it is not preferred to perform chemical vapor deposition treatment at the temperature over 1200°C .

[0041] As an organic matter desirable as a carbon source of chemical vapor deposition treatment Benzenetoluenexylenestyreneethylbenzenediphenylmethane Aromatic hydrocarbon of one ring such as diphenylnaphthalenephenolcresolnitrobenzenechlorobenzeneindenecumaronepyridineanthracene and phenanthrene thru/or three rings its derivative or its mixture is mentioned. Especially since it is hard to generate tar at the time of chemical vapor deposition treatment derivatives of an aromatic ring such as one benzenetoluenexylene and styrene are preferred.

[0042] Gas light oil creosote oil which are obtained by the distillation process of tar of a Carboniferous system Alcohol which is a derivative of aliphatic hydrocarbons such as anthracene oil the decomposition oil of a petroleum system naphtha-cracking tar oil methane ethane propane butane pentane and hexane and said aliphatic hydrocarbon is also independent or it can use as a mixture. The organic matter which has double bond such as acetylene ethylene propylene isopropanal pyrene and butadiene can also be used.

[0043] It is desirable still more preferred to consider it as the 2 - 30wt% on the basis of the graphite-grains child who becomes a core and the quantity of the carbon covered with a chemical-vapor-deposition-treatment method is 7 - 25wt%. carbon -- a graphite-grains child -- more than 2wt% -- by covering the decomposition depressant action of an

electrolysis solution solvent is revealed. When exceeding 30wt% the decomposition depressant action of an electrolysis solution solvent is saturated mostly and since adhesion of the graphite-grains children obtained becomes remarkable and tends to cause big and rough-ization of a negative pole material it is not desirable.

[0044] As for the organic matter as a carbon source supplied to a fluid bed reactor in chemical vapor deposition treatment it is preferred to supply with the form of the mixed gas diluted with inactive gas. Nitrogen, argon, etc. are mentioned as inactive gas. The ease of carrying out of acquisition or handling to especially nitrogen is preferred.

[0045] When performing chemical vapor deposition treatment using a fluid bed reactor inactive gas makes oxygen and an unreacted residual organic matter discharge from the inside of the system of reaction and it plays a role important also as a mobilization medium which forms a graphite-grains child's fluid bed.

[0046] The concentration of the organic matter in mixed gas has big influence on the crystallinity of vacuum evaporated carbon and molecular orientation to generate. The molar concentration of the desirable organic matter in mixed gas is 5 to 33% still more preferably 2 to 50%. By adjusting the organic substance concentration in mixed gas to the above-mentioned density range the vacuum-evaporated-carbon layer which has predetermined crystallinity and molecular orientation nature simply can be covered on the graphite-grains child surface. When the molar concentration of the organic matter in mixed gas is less than 2% the crystallinity of the carbon layer obtained by chemical vapor deposition treatment is high but the deposition rate of pyrolytic carbon is small and since chemical vapor deposition treatment takes a long time it is not desirable. On the other hand when the molar concentration of the organic matter in mixed gas exceeds 50% the deposition rate of pyrolytic carbon is large. However the crystallinity of the carbon layer obtained by vacuum evaporation falls and also the form of vacuum evaporated carbon grows the shape not of a film but fibrous or the shape of soot. For this reason to manufacture of the negative pole material of this invention aiming at covering the film of a uniform carbon layer to a graphite-grains child outside surface it is not desirable.

[0047] By choosing the above terms and conditions suitably and performing chemical vapor deposition treatment on the condition Average spacing d_{002} of the carbon layer which deposits on the graphite-grains child surface can be less than 0.337 nm and more desirable average spacing d_{002} of a covering carbon layer 0.3352-0.3369 nm and also more desirable average spacing d_{002} can be 0.3352-0.3359 nm. However it does not need for the average spacing of a carbon layer to be not necessarily in a mentioned range.

[0048] Next the above-mentioned negative pole material is observed using a transmission electron microscope etc. and it explains with reference to Drawings per [as a result of being obtained]. The feature of the carbon layer vapor-deposited on the graphite-grains child surface of the negative pole material is as follows.

[0049] Drawing 1 shows an example of the negative pole material of this invention. The negative pole material 6 shown in this typical sectional view consists of the approximately plate-like graphite-grains child 2 and the carbon layer 4 which covers that surface with carbon uniformly.

[0050] Drawing 2 is an enlarged drawing of the portion shown according to the boundary line A in drawing 1. The following knowledge will be acquired if the molecular orientation of the graphite-grains child 2 and the carbon layer 4 is examined in detail with reference to drawing 2.

[0051]As shown in drawing 2the approximately plate-like graphite-grains child 2 is covered with the side carbon layer 14 in the side (002nd page)and the upper surface (110th page) is covered with the upper surface carbon layer 16.

[0052]In drawing 2if it goes caudad from the upper partit irradiates with the electron beam X of a transmission electron microscope and the upper surface carbon layer 16 is observedthe clear lattice image of the 110th page of carbon is unobservable. Howeveraccording to the electron diffraction methodthe 110th page of carbon is observed.

[0053]If it goes caudad from the upper partit irradiates with the electron beam Y of a transmission electron microscope on the other hand and the side carbon layer 14 is observedthe clear lattice image of the 002nd page of carbon is observable. Thereforethe side carbon layer is making the crystal structure andmoreoverthat it is parallel to the graphite-grains child surface concludes theoretically the 110th page of carbon of the side carbon layer 14.

[0054]This audit observation means that the 110th page of carbon of the graphite-grains child surface is covered with the 110th page of carbon of a carbon layerand also that the 002nd page of carbon of the graphite-grains child surface is similarly covered with the 110th page of carbon of a carbon layer.

[0055]Thereforeit turns out that the negative pole material of this invention is a thing of the structure which covered all the surfaces of the graphite-grains child with the 110th page of carbon of the carbon layer.

[0056]Transmission electron microscope observation can also estimate the crystallinity of a vacuum-evaporated-carbon layerand molecular orientation via the interlayer spacing of the 002nd page of carbon.

[0057]⁷Li-NMR can be measured about what carried out the intercalation of the lithium ion to the above-mentioned negative pole materialand the measurement result of this ⁷Li-NMR can be used for structure evaluation of the above-mentioned negative pole material.

[0058]Specificallythe intercalation of the lithium ion is carried out to the anode formed using the negative pole material. Subsequently⁷Li-NMR measurement is performed about the anode which carried out the intercalation of the lithium ion. That in which a chemical shift has a composite spectrum which consists of an absorption spectrum of a 40-50 ppm position and an absorption spectrum of a 10-30 ppm position on a lithium-chloride standard (0 ppm) is preferred as a negative pole material for lithium secondary batteries.

[0059]Here the absorption spectrum of a 40-50 ppm position is an absorption spectrum originating in the lithium ion which carried out the intercalation to the high crystallinity graphite-grains child. The absorption spectrum of a 10-30 ppm position is a spectrum originating in the lithium ion which carried out the intercalation to the crystalline carbon layer. It is important that an absorption spectrum does not exist in existence of these two spectraan existence positionand a 90-120 ppm position as what the negative pole material of this invention is characterized and shows that especially a carbon layer is crystallinity.

[0060]On the other handalthough the intercalation of the lithium ion was carried out to the negative pole material which covered the amorphous carbon group to the graphite-grains childin a ⁷Li-NMR absorption spectruma 10-30 ppm absorption spectrum is not acceptedbut an absorption spectrum is observed at a 90-120 ppm position.

[0061]Although the intercalation of the lithium ion was carried out to the negative pole material which covered the low crystal carbon layer to the graphite-grains childan

absorption spectrum may be observed by the ^7Li -NMR absorption spectrum at a 10-30 ppm position and a 90-120 ppm position respectively.

[0062] All the surfaces of a graphite-grains child are covered with the 110th page of carbon of a carbon layer and the above-mentioned electron microscope and the measurement result of NMR show that the carbon layer is a crystalline carbon structure.

[0063] Therefore this invention can be defined as the carbon layer which can check the existence of the 110th page of carbon from the above-mentioned transmission electron microscope and the measurement result of NMR with a crystalline carbon layer.

[0064] The carbon layer of this invention negative pole material manufactured with chemical vapor deposition has the following character.

(1) It is greatly influenced by a graphite-grains child's molecular orientation and if the carbon made to cover with chemical vapor deposition treatment i.e. vacuum evaporated carbon has a graphite-grains child's small average interlaminar distance its average interlaminar distance of vacuum evaporated carbon is also small.

(2) The carbon layer vapor-deposited to the graphite-grains child is enough crystallized to such an extent that molecular orientation can be checked under a polarization microscope. The carbon layer vapor-deposited to the graphite-grains child is crystallized to such an extent that a crystallization organization can be enough checked also with a scanning type microscope.

(3) average spacing d_{002} of the carbon layer vapor-deposited to the graphite-grains child - - being completely [as a graphite-grains child's average spacing] the same -- ***** -- although it does not go it is a value very near a graphite-grains child's average spacing and is a slightly large value. Specifically average spacing d_{002} of the carbon layer are 0.3352-0.3369.

[0065] Drawing 3 shows an example of the fluid bed chemical vapor deposition system used when manufacturing the negative pole material of this invention.

[0066] As for a graphite-grains child in manufacturing the negative pole material of this invention it is preferred to carry out chemical vapor deposition treatment in the state where it mobilized. By mobilization supplying gas from the lower part of the reactor 42 and giving lift to particles here each graphite-grains child floats within the reactor 42 and the state of carrying out intense irregular movement is said. Since the graphite-grains child who mobilized has a clear interface in the upper part it is called the fluid bed or a fluid bed. A graphite-grains child's mobilized volume will be in the state where it expanded to about 1.2 to 1.6 times of the volume in the case of having settled in many cases.

[0067] As gas used for mobilization the mixed gas of the organic matter gas which is a carbon source or organic matter gas and inactive gas is preferred.

[0068] When mobilizing a graphite-grains child only by the flow of gas it is preferred to form a publicly known current plate (un-illustrating) in the lower part of the reactor 42 and to make it the flow of gas turn into a uniform flow to the section of the reactor 42. When the flow of gas is uneven the fluid bed cannot be held in the uniform state and when extreme it may flow so that the inside of the fluid bed may be foamed or gas produces a specific gas passageway (rat hole) and may not form the fluid bed.

[0069] In this invention a graphite-grains child may be mobilized only by the flow of gas. However when the fluid bed which originated in the graphite-grains child's description and was stabilized is not obtained it is preferred to form the agitator 40 in the inside of the

reactor 42 and to stir a graphite-grains child. The fluid bed uniform thereby more certainly can be formed. As for the peripheral velocity in the tip of the agitating blade 41 in vapor-depositing a carbon layer to a graphite-grains child the amount of 250-20000-cm/s is desirable. Although based also on deposition treatment conditions such as reaction temperature when peripheral velocity is the following by 250-cm/s it becomes easy to cause deposition of carbon to an agitating blade. Since scattering of particles increases and yield falls when peripheral velocity exceeds a part for 20000-cm/s it is not desirable.

[0070] The uniform fluid bed can be formed by forming the agitator 40 and attaching a shaker (un-illustrating) to the exterior of the reactor 42 vibrating the reactor 42 and giving a graphite-grains child vibration indirectly instead of forming the agitator 40. Although vibration changes with scales of the reactor 42 etc. it is preferred to consider it for example as the resonance frequency of 2-30 Hertz of a system and the amplitude of 0.2-30 mm. This vibration can be easily generated with the usual electromotive shaker.

[0071] A batch process or continuous system can also perform operation of deposition treatment. In the case of a batch process a graphite-grains child is supplied in the reactor 42 from the black lead hopper 22. In the case of continuous system although there is no restriction in the feeding means it can supply in the reactor 42 using a fixed-quantity-type screw feeder (un-illustrating) for example. Since a graphite-grains child is in the mobilized state of complete mixing within the reactor 42 the position in particular that supplies a graphite-grains child in the reactor 42 does not have restriction. By carrying out chemical vapor deposition treatment of the graphite-grains child in this state where it mobilized the negative pole material of this invention generates in the reactor 42.

[0072] There are a method of extracting a negative pole material by a screw feeder etc. of a fixed-quantity type which connected a generated negative pole material with the negative pole material extraction hole 46 for example as a method of making it discharge continuously out of the reactor 42 etc. There is a method of making overflow a negative pole material and taking out from the upper part of the fluid bed besides this.

[0073] Since heat transfer of the fluid bed is dramatically good in order to carry out temperature up of the fluid bed to a predetermined chemical-vapor-deposition-treatment temperature it is enough if it usually heats by the electric heater 44 from the exterior of the reactor 42. However mixed gas may be preheated as occasion demands.

[0074] the inside of drawing 3 and 24 -- a carbon source and 26 -- a fixed quantity -- a liquid pump and 28 -- carbon source liquid sending lines and 30 -- as for gas flowmeter and 38 gas flowmeter and 34 are [a bag filter and 50] exhaust lines inactive gas lines and 48 a source mixing line of inactive gas carbon matter and 36 inactive gas and 32.

[0075] As mentioned above a graphite-grains child's mean particle diameter has a 1-100-micrometer preferred thing. This particle diameter is especially preferred when performing chemical vapor deposition treatment using a fluidized bed reactor. When a graphite-grains child's mean particle diameter is less than 1 micrometer it is substantially difficult to cover a graphite-grains child with a carbon layer thoroughly and since quantity of a graphite-grains child who disperses out of the system of reaction according to a gas stream increases and yield of a negative pole material falls it is not desirable. On the other hand if mean particle diameter exceeds 100 micrometers since formation of the uniform fluid bed may become difficult it is not desirable.

[0076] A graphite-grains child's true density is about 2g/cm^3 . The desirable range of the bulk density of the graphite-grains child in the mobilization state under chemical vapor

deposition treatment is a 0.1 - 0.5 g/cm³ grade. Chemical vapor deposition treatment tends to be uniformly performed so that the bulk density of the graphite-grains child of a mobilization state is low. However when the graphite-grains child of a mobilization state is [bulk density] less than 0.1 g/cm³ even if it reduces bulk density further improvement in equalization of vacuum evaporation becomes is hard to be carried out in proportion to it. Rather in order to make bulk density low larger equipment is needed and since it comes to need many energies in order for the gas volume supplied in order to make a graphite-grains child mobilize to increase and to heat the gas along with it it is not desirable. On the other hand when the bulk density of the graphite-grains child of a mobilization state exceeds 0.5 g/cm³ in a reactor gas carries out channeling and cannot maintain a graphite-grains child's uniform mobilization condition easily. For this reason it becomes difficult to perform uniformly a graphite-grains child's chemical vapor deposition treatment.

[0077] The chemical vapor deposition treatment performed in the fluid bed of the above-mentioned bulk density is seen from the volume share of the particles in reactor space as shown below and he can understand that it is desirable processing environment. For example since the true density of the graphite-grains child who uses is about 2g/cm³ when a graphite-grains child forms the good mobilization state of bulk density 0.2 g/cm³ in deposition treatment the volume share of the graphite-grains child in reactor space becomes 10 volume %. Therefore 90 volume % in a reactor will be occupied by gas and this will occupy the child 9 times the volume of graphite grains. For this reason a graphite-grains child will do intense irregular movement in the state where it was held in space large enough. In the chemical vapor deposition treatment in this mobilization state gas-particle contact is fully attained gas-particle contacting efficiency becomes high and as a result the conversion rate to a carbon layer will become high from an organic matter. The obtained vacuum evaporation film will also become uniform. Since the gas-particle contact area is performed by the fluid bed sufficient large space for a graphite-grains child to do irregular motion violently is secured. For this reason troubles such as graphite-grains children's adhesion are also avoidable. On the other hand deposition treatment of the conventional chemical vapor deposition treatment is carried out in the state where it settled. Therefore gas-particle contacting efficiency is low and moreover it is easy to produce troubles such as adhesion between graphite-grains children.

[0078] As equipment which carries out chemical vapor deposition treatment of the negative pole material of this invention in the state of mobilization and manufactures it if it is a fluid bed chemical vapor deposition system the fluid bed chemical vapor deposition system of various styles can be used.

[0079] Drawing 4 shows another example of the fluid bed chemical vapor deposition system which manufactures the negative pole material of this invention.

[0080] In drawing 4 the reactor 84 is a continuous system vertical-type reactor and can heat the inside of the reactor 84 by the electric heater 86 which covered and attached the exterior of the reactor 84. The electric shaker 82 is formed in the outside of the reactor 84 lower part. In fixed quantity by the feeder 64 the graphite-grains child in the tank 62 is seen off in the reactor 84 lower part and is supplied in the reactor 84 from here. The negative pole material which is output is discharged by the output acceptor 90 through the output extraction line 88 from the upper part of the reactor 84.

[0081] On the other hand the organic matter as the carbon source 66 is supplied to reactor 84 inside from the lower part of the reactor 84 through the carbon source liquid sending

lines 70 by the liquid pump 68 in fixed quantity. The inactive gas 72 is supplied in the reactor 84 from the inactive gas lines 80 connected with the lower part of the reactor 84. Thereby the particles in the reactor 84 are made to mobilize. The graphite-grains child in the reactor 84 is vibrated by operating the electric shaker 82. The mobilization state where the graphite-grains child (un-illustrating) in the reactor 84 was stabilized is made to form by these operations. A carbon layer is covered with the above operation to a graphite-grains child and a negative pole material is obtained.

[0082] As for the source mixing line of inactive gas carbon matter and 7874 are [a bag filter and 94] exhaust lines gas flowmeter and 92 gas flowmeter and 76 among drawing 4.

[0083] Drawing 5 shows another example of the fluid bed equipment which manufactures the negative pole material of this invention.

[0084] In drawing 5 the reactor 124 is a continuous system vertical-type reactor. An inside of the reactor 124 can be heated by the electric heater 126 which covered and attached the exterior of the reactor 124. The electric shaker 122 is formed in the exterior of the reactor 124 lower part. A graphite-grains child is supplied in the reactor 124 from the reactor 124 upper part by the feeder 104 in fixed quantity from the tank 102. A negative pole material which is output is discharged by the output acceptor 130 through the output extraction line 128 from the lower part of the reactor 124.

[0085] On the other hand an organic matter as the carbon source 106 is supplied from the lower part of the reactor 124 through the carbon source liquid sending lines 110 in reactor 124 inside by the liquid pump 108 in fixed quantity. The inactive gas 112 is supplied in the reactor 124 from the inactive gas lines 120 provided in the lower part of the reactor 124. By supply of this inactive gas a graphite-grains child in the reactor 124 is made to mobilize and a graphite-grains child in the reactor 124 is vibrated by operating the electric shaker 122. Thereby a mobilization state where a graphite-grains child (un-illustrating) in the reactor 124 was stabilized is made to form. A carbon layer is covered with the above operation to a graphite-grains child and a negative pole material is obtained.

[0086] As for the source mixing line of inactive gas carbon matter and 118114 are [a bag filter and 134] exhaust lines gas flowmeter and 132 gas flowmeter and 116 among drawing 5. Although the method in particular of preparing the anode of a rechargeable lithium-ion battery is not limited using the negative pole material of this invention manufactured as mentioned above the example is shown below.

[0087] The solvent (for example 1-methyl-2-pyrrolidone) which dissolved the binder (for example PVDF: polyvinylidene fluoride) in the negative pole material is added and it fully mulls. By this operation the high-concentration negative pole material slurry beyond negative pole material concentration 40wt% can be prepared. A doctor blade etc. are used for the charge collector which consists this negative pole material slurry of metallic foils (for example copper foil) and a thickness of 20-100 micrometers is coated. By drying this negative pole material particles stick to a metal foil collector. It pressurizes if necessary and adhesion is improved and the thickness of a coating layer is equalized. A publicly known material for example various kinds of pitches rubber a synthetic resin etc. can be used for a binder. PVDF EPDM (ethylene propylene diene monomer) and carboxymethyl cellulose (CMC) are preferred also in these. As for the mixture ratio (weight ratio) of a negative pole material and a binder being referred to as 100:2-100:20 is desirable.

[0088] Although a positive electrode material in particular is not limited lithium contained

compounds such as publicly known LiCoO_2 , LiNiO_2 or LiMn_2O_4 or these mixtures are suitable for a person skilled in the art. If a powdered positive electrode material has necessity it will add a conducting material fully fabricated [solvent / which dissolved the binder] after a mull and with a charge collector and can prepare it. There is no limitation in particular also about a separator and a publicly known material can be used. [0089] As a nonaqueous solvent which is a main solvent of an electrolysis solution the publicly known solvent of an aprotic lower dielectric constant which dissolves lithium salt is mentioned. For example ethylene carbonate, dimethyl carbonate (it abbreviates to DMC below), methyl ethyl carbonate (it omits the following MEC), propylene carbonate, diethylene carbonate, acetonitrile, propionitrile, tetrahydrofuran, gamma-butyrolactone, 2-methyltetrahydrofuran, 1,3-dioxolane, The 4-methyl-1,3-dioxolane, 1,2-dimethoxyethane, 1,2-diethoxyethane. It is independent about solvents such as diethylethers, sulfolane, methyl sulfolane, nitromethane, N,N-dimethylformamide and dimethyl sulfoxide or two or more sorts of solvents can be mixed and used.

[0090] As lithium salt used as an electrolyte LiClO_4 , LiAsF_6 , There are LiPF_6 , LiBF_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCl , LiBr , $\text{CH}_3\text{SO}_3\text{Li}$, $\text{CF}_3\text{SO}_3\text{Li}$ etc. independence or two or more kinds of salts can be mixed and these salts can be used.

[0091] It can also be considered as a lithium polymer secondary battery using polymer electrolyte such as a gel electrolyte which gelled the nonaqueous solvent which is a main solvent of the above-mentioned electrolysis solution and the electrolyte polyethylene oxide or polyacrylonitrile etc.

[0092] A totally-solid lithium secondary battery can also be manufactured using a solid electrolyte.

[0093] The composition of these rechargeable batteries itself is publicly known.

[0094] Hereafter an embodiment explains this invention still more concretely.

[0095]

[Working example] In the following Embodiments 1-4 and the comparative example 1 each property value was measured by the following methods.

[0096] The amount of vacuum evaporated carbon: Using Shimadzu thermo gravity analysis apparatus GDT-50 reduction in weight was measured in airstream and a part for the clearly different weight loss from base material black lead was made into the amount of vacuum evaporated carbon.

[0097] Mean particle diameter: It measured using Shimadzu laser diffraction type size distribution measuring device SALD1100.

[0098] Specific surface area: Using the Japanese bell tabulation area measuring device the amount of nitrogen absorption was measured by the multipoint method with liquid nitrogen temperature and specific surface area was determined with the BET adsorption method.

[0099] Tap density: The value which put in and tapped the sample to 100-ml glass measuring cylinders measured sample capacity in the place where the capacity of a sample will not change and $\frac{\text{sample weight}}{\text{sample capacity}}$ was made into tap density.

[0100] Average spacing d_{002} : Using Toshiba X-ray diffractometer XC-40H Cu-K alpha rays were monochrome-ized with nickel and it measured with Gakushin method by using high purity silicon as a standard substance.

[0101] (Embodiments 1-4 comparative example 1) Compression grinding of the natural

graphite from Brazil was carried out with the oscillating rod mill and the graphite-grains child with a particle diameter of 45 micrometers or less (mean particle diameter of 18 micrometers) was obtained. Thermochemistry deposition treatment of this graphite-grains child was carried out using the fluid bed reactor 22 shown in drawing 3.

[0102] In drawing 3 the reactor 42 is a batch type vertical-type reactor of 100 mm in diameter and 300 mm of heating unit tube length and can heat the inside of the reactor 42 by the electric heater 44 which covered and attached the exterior of the reactor 42. The agitator 40 was formed in the inside of the reactor 42. The graphite-grains child 500g was supplied in the reactor 42 from the hopper 22. After supplying a graphite-grains child in the reactor 42 it let the inactive gas lines 38 provided in the lower part of the reactor 42 pass and nitrogen was supplied by the flow of 1 L/min as the inactive gas 30 in the reactor 42. After it carried out temperature up of the inside of the reactor 42 in this state and the inside of the reactor 42 reached 900 °C benzene was supplied to the lower part of the reactor 42 by the flow of 2 mL/min as the carbon source 24 using the fixed-quantity liquid pump 26.

[0103] The graphite-grains child in the reactor 42 was made to mobilize according to the gas stream which flows through the inside of the reactor 42 upwards from a lower part and the graphite-grains child in the reactor 42 was stirred by operating the agitator 40 by a part for agitating blade tip peripheral velocity of 1200 cm. This formed the mobilization state where the graphite-grains child (un-illustrating) in the reactor 42 was stabilized. this state -- a graphite-grains child -- predetermined time thermochemistry deposition treatment -- it carried out. After processing of one batch of predetermined time was completed output was made to discharge from the output extraction hole 46 provided in the lower part of the reactor 42.

[0104] About the 45-micrometer minus sieve sample of the obtained negative pole material the evaluation test as a negative pole material for rechargeable lithium-ion batteries was done on condition of Table 1. The evaluation test result is shown in Table 2.

[0105]

[Table 1]

*1 PVDF: polyvinylidene fluoride *2 PC: -- propylene carbonate *3 MEC: methylethyl carbonate *4 EC: ethylene carbonate *5 DMC: -- dimethyl carbonate [0106]

[Table 2]

*1 Graphite-grains child *2 which is not performing chemical vapor deposition treatment It is a value of the average spacing of black lead.

As shown in Table 2 average spacing d_{002} of a carbon layer of the negative pole material of Embodiments 1-4 is less than 0.337 nm.

The audit observation of NMR and an electron microscope to the graphite-grains child was the negative pole material covered with the crystalline carbon layer.

And as shown in a charge and discharge test result these negative pole materials have high service capacity and high coulomb efficiency without disassembling an electrolysis solution solvent.

[0107] The negative pole material of Embodiment 3 was embedded at polyester resin

ground with the conventional method and the organization was observed under the reflective polarization microscope. As shown in drawing 6 the negative pole material deposited with the molecular orientation as the graphite-grains child of a base material where the carbon layer which showed optical anisotropy and was vapor-deposited is the same in all the portions and the result checked having covered the graphite-grains child. [0108] (Embodiment 5) The manufacture positive active material (LiCoO_2) of a real cell and a conducting material (artificial graphite) were mixed by 9:1 (weight reference). this -- PVDF -- 5wt% -- the 1-methyl-2-pyrrolidone solution to contain was distributed and the LiCoO_2 slurry was prepared. After applying the slurry to 60 micrometers in thickness on aluminium foil using a doctor blade it dried at 130 °C for 2 hours and the cathode was prepared.

[0109] the negative pole material of Embodiment 3 -- PVDF -- 9wt% -- the 1-methyl-2-pyrrolidone solution to contain was distributed and negative pole material concentration 65wt% of the slurry was prepared. The obtained negative pole material slurry was applied to 30 micrometers in thickness on copper foil using the doctor blade was dried at 130 °C for 2 hours and the anode was prepared.

[0110] Celgard by a Cera-Needs company was used as a separator. The cathode and the anode were laminated and rolled round via the separator and this was put into the stainless steel can which served as the anode. After pouring into a negative electrode can the solution of PC / methyl carbonate / EC (volume ratio 1:1:1.5) which dissolved LiPF_6 of concentration 1 M/L as an electrolyte it covered with the cathode lid and the rechargeable lithium-ion battery was manufactured.

[0111] The charge and discharge of this cell were carried out between the potential of 4.2V and 2.7V at 200 mA using this cell. As a result the volume energy density of this cell was 377 Wh/L. Although 1000 charges and discharges were performed the 1000th discharging amount was 92% of a first-time discharging amount. As compared with 25 °C service capacity 60 °C service capacity was 102% and 0 °C service capacity was 98%. In the following Embodiments 6 and the comparative examples 2 and 3 each property value was measured by the following methods.

[0112] The amount of vacuum evaporated carbon: Using Shimadzu thermo gravity analysis apparatus GDT-50 weight loss was measured under airstream and a part for the clearly different weight loss from base material black lead was made into the amount of vacuum evaporated carbon.

[0113] Mean particle diameter: It measured using Shimadzu laser diffraction type size distribution measuring device SALD1100.

[0114] Specific surface area: Using Japanese bell tabulation area measuring device BELSORB28 the amount of nitrogen absorption was measured by the multipoint method with liquid nitrogen temperature and specific surface area was determined with the BET adsorption method.

[0115] Tap density: The value which put in and tapped the sample to 100-ml glass measuring cylinders measured sample capacity in the place where the capacity of a sample will not change and (g/cc) sample weight to sample capacity was made into tap density.

[0116] Average spacing d_{002} : Using product X-ray diffractometer LINT made from physical science 1111 Cu-K alpha rays were monochrome-ized with nickel and it measured with Gakushin method by using high purity silicon as a standard substance.

[0117]A transmission electron microscope and electron diffraction: Light field image photography and electron diffraction measurement were performed using JEOL transmission electron microscope 2000FX.

[0118] ^7Li solid NMR : Bruker solid-state-nuclear-magnetic-resonance equipment DSX300wb was equipped with the polynuclear kind double width probe head and it measured by making lithium-chloride solution into a standard.

[0119](Embodiment 6) After carrying out compression grinding of the natural graphite from Brazil with an oscillating rod mill it sifted out at 53 micrometers and the graphite-grains child of tap density 0.800 g/cm^3 which is the minus sieve was obtained.

Subsequently although sizes differed from carried out thermochemistry deposition treatment of the above-mentioned graphite-grains child using the fluid bed reactor 42 shown in the same drawing 3.

[0120] In drawing 3 the reactor 42 is a batch type vertical-type reactor of 500 mm in diameter and 1500 mm of heating unit tube length and can heat the inside of the reactor 42 by the electric heater 44 which covered and attached the exterior of the reactor 42. The agitator 40 was formed in the inside of the reactor 42. 60 kg of graphite-grains children were supplied in the reactor 42 from the hopper 22.

[0121] The graphite-grains child was supplied in the reactor 42 and the nitrogen 30 was supplied by the flow of 50 L/min as inactive gas in the reactor 42 through the inactive gas lines 38 provided in the lower part of the reactor 42. Temperature up of the inside of the reactor 42 was carried out in this state. After the inside of the reactor 42 reached 1000

**toluene was supplied to the lower part of the reactor 42 by the flow of 158 mL/min using the liquid pump 26 for a fixed quantity as the carbon source 24 (molar concentration of toluene in toluene-nitrogen mixed gas: 40%). The graphite-grains child in the reactor 42 was made to mobilize according to the gas stream which flows through the inside of the reactor 42 upwards from a lower part. The agitator 40 was operated by a part for agitating blade tip peripheral velocity of 1200 cm and this stirred the graphite-grains child in the reactor 42. This formed the mobilization state where the graphite-grains child (un-illustrating) in the reactor 42 was stabilized. Chemical vapor deposition treatment of the graphite-grains child was carried out for 120 minutes in this state. After processing of this one batch was completed output was made to discharge from the output extraction hole 46 provided in the lower part of the reactor 42.

[0122] About the 53-micrometer minus sieve sample of the obtained negative pole material the evaluation test as a negative pole material for rechargeable lithium-ion batteries was done on condition of Table 3. The evaluation test result is shown in Table 4.

[0123]

[Table 3]

*1 PVDF: -- polyvinylidene fluoride *2 PC: propylene carbonate *3 EC: ethylene carbonate *4 MEC: -- methylethyl carbonate [0124]

[Table 4]

*1 Heat-treating-time *2 for the formation of a covering pitch coal The peak conducted the structural analysis of the carbon layer of the negative pole material of the incapable

measurement embodiment 6 with the electron diffraction method using a transmission electron microscope with broadcloth. A negative pole material is plate-like form shown in drawing 1. The transmission electron microscope photograph of this negative pole material is shown in drawing 7. As shown in the transmission electron microscope photograph of drawing 7 the plaid of the 002nd page of clear carbon was observed in the carbon layer of the negative pole material. This plaid interval i.e. the average spacing of the 002nd page of carbon was 0.33645 nm. The electron diffraction photograph which irradiated with and obtained the electron beam to the plane direction (the direction of Y of drawing 2) of this side carbon layer 14 is shown in drawing 8. Drawing 8 shows the 002nd page of carbon of crystalline carbon.

[0125] Also about the upper surface carbon layer 16 formed in the plate shaped part of the upper surface of this negative pole material the field of the upper surface carbon layer was irradiated with the electron beam of the transmission electron microscope perpendicularly (the direction of X of drawing 2) and the electron diffraction photograph was obtained. The photograph showed the 110th page of carbon of crystalline carbon.

[0126] Next the measurement result of ^7Li -NMR of the negative pole material of a charging state (state which carried out the intercalation of the lithium ion to the negative pole material) is shown in drawing 9. The lithium ion which carried out the intercalation to 42.9 ppm at natural graphite was observed. The lithium ion by which occlusion was carried out to 15.1 ppm or it carried out the intercalation to crystalline carbon was observed.

[0127] A graphite-grains child makes parallel a graphite-grains child's surface and the 110th page of carbon of a carbon layer and is covered with a carbon layer and it is clear from the above result that a covering carbon layer's it is crystallinity.

[0128] (Comparative example 2) The graphite-grains child 10g who used in Embodiment 6 was taught to the fixed-bed chemical-vacuum-deposition reactor and chemical vapor deposition treatment was performed using the toluene-nitrogen mixed gas of the same concentration (40-mol %) as Embodiment 6. About the obtained negative pole material the evaluation test as a negative pole material for rechargeable lithium-ion batteries was done on condition of Table 3. The evaluation test result is shown in Table 4. As shown in Table 4 it is clear that the negative pole material's manufactured with fixed-bed chemical vapor deposition the carbon coating of the graphite-grains child surface is imperfect.

[0129] A fixed-bed chemical-vacuum-deposition reactor attaches a black lead board in the cylindrical reactor made from quartz. The graphite-grains child was heaped up to said black lead tabular and mixed gas was supplied heating from the reactor outside. 95 mm in diameter 800 mm in length and the black lead board of the reactor were plate-like [95 mm x 120 mm]. Evaporation temperature was 1000 **.

[0130] (Comparative example 3) With the graphite-grains child 100g who used in Embodiment 6 at 320 ** it cooled after the mull and subsequently the meso face pitch of 25 g of coal tar pitch origin (295 ** of softening temperature amount of fixed carbon content 82wt%) was ground. This was heated under 30-minute interspace mind circulation at 330 ** and it performed non-deliquest [of the covering pitch]. Then temperature up was carried out to 1000 ** by the heating rate of 10 ** / min. Subsequently heat treatment was performed for 120 minutes at the temperature and the negative pole material was prepared. About the obtained negative pole material the

evaluation test as a negative pole material for rechargeable lithium-ion batteries was done on condition of Table 3. The evaluation test result is shown in Table 4. As shown in Table 4 it is clear that the negative pole material's which was carbonized after mulling a graphite-grains child and a pitch and was manufactured the carbon coating of the graphite-grains child surface is imperfect.

[0131] Drawing 10 shows the absorption spectrum of ^7Li -NMR of the negative pole material of the comparative example 3 of a charging state (state which carried out the intercalation of the lithium ion to the negative pole material). According to this absorption spectrum the absorption spectrum originating in the lithium ion in which the absorption spectrum originating in the lithium ion which carried out the intercalation to a 15 ppm position at crystalline carbon carried out the intercalation to a 110 ppm position again at isotropic carbon is accepted.

[0132] As mentioned above the vacuum-evaporated-carbon layer which covered the graphite-grains child of Embodiment 6 with fluid bed chemical vapor deposition is a crystalline carbon layer which has covered all the surfaces of a graphite-grains child with the 110th page of carbon.

[0133] The vacuum evaporated carbon which on the other hand covered the graphite-grains child of the comparative example 2 with fixed-bed chemical vapor deposition and the covering carbon carbonized after mulling the graphite-grains child and pitch of the comparative example 3 have imperfect covering by carbon of the graphite-grains child surface.

[0134] The above fact is the knowledge which was not expected at all from the conventional negative pole material which uses as the negative pole material for rechargeable lithium-ion batteries the graphite-grains child who covered with the low crystal carbon layer.

[0135] On the other hand according to the chemical-vapor-deposition-treatment method which adopts a fluid bed since the graphite-grains child has set to the floating state with the cracked gas of said organic matter further with the organic matter used as a carbon source and the inactive gas made to live together as occasion demands the surfaces of all the are uniformly covered by these gases. For this reason all the surfaces of a graphite-grains child can be covered with a small amount of carbon uniformly and thoroughly.

[0136] It is the structure in which this carbon layer covered all the surfaces of the graphite-grains child with the 110th page of carbon of the carbon layer in addition to this carbon layer of the negative pole material produced by setting up terms and conditions appropriately in the describing [above] fluid bed chemical-vapor-deposition-treatment method being crystallinity. And even if it forms a carbon layer more thinly than before all the surfaces of a graphite-grains child can be covered uniformly and thoroughly. Since there are few (2) covering carbon contents from which a still higher charge-and-discharge speed is obtained since there are few (1) covering carbon contents as the result the rate that black lead in a negative pole material occupies is high. For this reason in order to cover uniformly and thoroughly with a carbon layer all the surfaces of (3) graphite-grains child who has high service capacity and to cover uniformly and thoroughly all the surfaces of (4) graphite-grains child with high coulomb efficiency with a carbon layer disassembly of solvent such as PC is controlled. For this reason there is an advantage of the cell formed using this negative pole material preventing the danger of the explosion based on the cracked gas of a solvent.

[0137]The conventional knowledge which uses as the negative pole material for rechargeable lithium-ion batteries the black lead which covered the above advantages with low crystal carbon to a graphite-grains childIt is not expected at all from the negative pole material obtained also from the negative pole material which consists of vacuum evaporated carbon which covered this graphite-grains child with fixed-bed chemical vapor deposition by carbonizing after mulling a graphite-grains child and a pitch.

[0138]

[Effect of the Invention]Since the negative pole material for lithium secondary batteries of this invention serves as a graphite-grains child from the carbon layer which covered the graphite-grains child's surface with the 110th page of carbon with crystalline carbon using the chemical-vapor-deposition-treatment methodHigh-speed charge and discharge are possible for the lithium secondary battery manufactured using thisits service capacity is largeand its coulomb efficiency is highand it is excellent in the low-temperature characteristicthe elevated-temperature characteristicetc.

Disassembly of solventssuch as PCis controlleda cell is protected from explosionand it has the advantage of making it a safe thing.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a typical sectional view showing an example of the negative pole material for lithium secondary batteries of this invention.

[Drawing 2]It is an enlarged drawing of the portion A of the negative pole material shown in drawing 1.

[Drawing 3]It is a schematic view showing an example of the chemical-vapor-deposition-treatment equipment for negative pole material manufacture of this invention for lithium secondary batteries.

[Drawing 4]It is a schematic view showing another example of the chemical-vapor-deposition-treatment equipment for negative pole material manufacture of this invention for lithium secondary batteries.

[Drawing 5]It is a schematic view showing another example of the chemical-vapor-deposition-treatment equipment for negative pole material manufacture of this invention for lithium secondary batteries.

[Drawing 6]It is a polarization electron microscope photograph in which an example of the negative pole material for lithium secondary batteries of this invention is shown.

[Drawing 7]It is a transmission electron microscope photograph which shows an example of the negative pole material for lithium secondary batteries of this invention.

[Drawing 8]It is an electron diffraction photograph which shows an example of the negative pole material for lithium secondary batteries of this invention.

[Drawing 9]It is a ^7Li -NMR spectrum in which an example of the negative pole material for lithium secondary batteries of this invention which carried out the intercalation of the lithium ion is shown.

[Drawing 10]It is a ^7Li -NMR spectrum in which the negative pole material for lithium

secondary batteries of the comparative example 3 which carried out the intercalation of the lithium ion is shown.

[Explanations of letters or numerals]

- 2 Graphite-grains child
- 4 Covering carbon layer
- 6 Negative pole material
- 14 Side carbon layer
- 16 Upper surface carbon layer
- 22 Black lead hopper
- 24 Carbon source
- 26 Fixed-quantity liquid pump
- 28 Carbon source liquid sending lines
- 30 Inactive gas
- 32 Gas flowmeter
- 34 Source mixing line of inactive gas carbon matter
- 36 Gas flowmeter
- 38 Inactive gas lines
- 40 Agitator
- 41 Agitating blade
- 42 Reactor
- 44 Electric heater
- 46 Negative pole material extraction hole
- 48 Bag filter
- 50 Exhaust line
- 62 Tank
- 64 Fixed-quantity feeder
- 66 Carbon source
- 68 Fixed-quantity liquid pump
- 70 Carbon source liquid sending lines
- 72 Inactive gas
- 74 Gas flowmeter
- 76 Source mixing line of inactive gas carbon matter
- 78 Gas flowmeter
- 80 Inactive gas lines
- 82 Electric-oscillation machine
- 84 Reactor
- 86 Electric heater
- 88 Output extraction line
- 90 Output acceptor
- 92 Bag filter
- 94 Exhaust line
- 102 Tank
- 104 Fixed-quantity feeder
- 106 Carbon source
- 108 Fixed-quantity liquid pump
- 110 Carbon source liquid sending lines

112 Inactive gas
114 Gas flowmeter
116 Source mixing line of inactive gas carbon matter
118 Gas flowmeter
120 Inactive gas lines
122 Electric-oscillation machine
124 Reactor
126 Electric heater
128 Output extraction feeder
130 Output acceptor
132 Bag filter
134 Exhaust line
